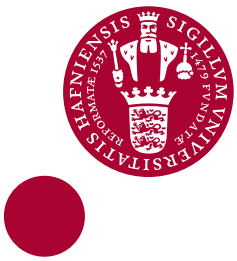

NMR studies of stock process water and reaction pathways in hydrothermal carbonization of furfural residue

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Research paper

NMR studies of stock process water and reaction pathways in hydrothermal carbonization of furfural residue

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Abstract

Hydrothermal carbonization (HTC) is a valuable approach to convert furfural residue (FR) into carbon material. The prepared biochars are usually characterized comprehensively, while the stock process water still remains to be studied in detail. Herein, a NMR study of the main components in stock process water generated at different HTC reaction conditions was reported. Various qualitative and quantitative NMR techniques (^{1}H and ^{13}C NMR, ^{1}H−^{1}H COSY and ^{1}H−^{13}C HSQC *etc.*) especially 1D selective gradient total correlation spectroscopy (TOCSY NMR) were strategically applied in the analysis of HTC stock process water. Without separation and purification, it was demonstrated that the main detectable compounds are 5-hydroxymethylfurfural, formic acid, methanol, acetic acid, levulinic acid, glycerol, hydroxyacetone and acetaldehyde in this complicate mixture. Furthermore, the relationship between the concentration of major products and the reaction conditions (180−240 °C at 8 h, and 1−24 h at 240 °C) was established. Finally, reasonable reaction pathways for hydrothermal conversion of FR were proposed based on this result and our previously obtained characteristics of biochars. The routine and challenging NMR methods utilized here would be an alternative other than HPLC or GC for biomass conversion research and can be extended to more studies.

Keywords: NMR; Hydrothermal carbonization; Furfural residue; Stock process water

1. Introduction

Furfural residue (FR) is an acidic solid waste generated in the furfural production industrial process, and is mainly composed of cellulose and lignin. Plentiful but low valuable FR was produced annually, and it would be inspiring if economical and sustainable methods could be developed to upgrade FR [1]. One of the most promising ways is converting FR into carbon materials because of its high carbon content (more than 40% in weight) [2]. Hydrothermal carbonization (HTC) is an environment friendly thermochemical processing technique, which can efficiently convert lignocellulose biomass into biochars with a high energy density and therefore is widely used nowadays [3,4]. During HTC process, biomass is usually treated in hot compressed water (i.e. 180−280 °C) with saturated vapor pressures at the range from 2 to 10 MPa [5], and then solid products (biochars) would be gathered for using as absorbents, supercapacitor electrodes, and catalysts *etc.* [4,6].

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Most researches are focused on the properties of biochars prepared at different HTC conditions and its formation mechanism in HTC process [7]. It is generally accepted that reaction types involved in the HTC of lignocellulose mainly are hydrolysis, dehydration, isomerization, aldol condensation and reforming [5]. There are two reaction schemes of HTC reported. The first one, Sevilla et al. [8] described a mechanism of cellulose HTC according to the characterization of biochar and the former works on cellulose transformations under sub- or supercritical water [9], and the main reactions are involved including hydrolysis, dehydration and fragmentation, polymerization, aromatization, nucleation and the growth of solid nuclei. For another scheme, Titirici et al. [10] analysis the biochar structure by solid state NMR, and reported that the cellulose HTC process is to transform feedstock into an aromatic carbon network directly and which is similar with a classical pyrolysis, even if the exact chemical paths are not clear yet. All studies mentioned above are focused on the structure of solid biochar, while only a few systematically investigated the composition of the stock process water due to its complexity.

Essentially, detailed investigation of HTC stock process water is necessary for providing more precise information on the mechanism and reaction pathway, and it can be guideline to industry for disposal or treating huge amount HTC liquids properly [11,12]. As a complex mixture of by-products, individual organic toxic compounds found in process water are often observed with the concentration up to several grams per liter. These organic acids will guarantee drinking water safety, national welfare and people's livelihood, and facilitate the sustainable development of human health and economic stability [13]. For the possible compounds in aqueous phase, 5-hydroxymethylfurfural (5-HMF) is a well-known platform molecule and shows the potential to be isolated and converted to biofuel [14]. Presently, the process water is roughly evaluated for its possible environmental impact through the measurement of total organic carbon (TOC) as a summation parameter [15]. Typically the waste water contains phenols, furfurals, 5-hydroxymethylfurfural (5-HMF) and other derivatives derived from lignocellulosic biomass [16]. But till now, only few studies were related with the biomass (no FR yet) HTC stock process water, and gas chromatography (GC) [17] or high performance liquid chromatography (HPLC) [18] were usually used. Standard compounds are essential for running HPLC analysis, and it is very difficult to choose them without the knowledge of what reactions happened in HTC. As reported, many reactions happened simultaneously in HTC and different compounds yielded from different feedstocks [19,20], and the stock process water contains up to 15% of carbon depending on the reaction conditions [7], so GC or HPLC would be limited if no standard compounds available as well as the reactions are too complicate.

Actually, as a non-invasive and informative technology, NMR plays an important role in biomass conversion researches, it can provide structural besides quantitative information of major compounds and even reaction intermediates at the same time. The solid state NMR has been extensively utilized in the structural analysis of biochar and mechanism studies of the HTC of lignocellulosic biomass [21,22]. While as for the liquid phase, Berge et al. [7] employed ^{1}H NMR for cellulose HTC liquid samples, and the main compounds were assigned according to the other report, and Sun et al. [23] found 4-hydroxy-4-methyl-2-pentanone in the acetone-soluble sample of HTC bamboo also using ^{1}H NMR. Our recent studies showed that NMR is a versatile method to study the biomass conversion, which can provide structural information qualitatively and quantify the product yields [24], and can also acquire more detailed information under the reaction conditions without the need for quenching the reaction [25].

Therefore, it is worth trying NMR technology to investigate the stock process water of FR HTC without purification. Firstly, various NMR methods including ^{1}H NMR, ^{13}C NMR, ^{1}H–^{1}H correlation spectroscopy (COSY), ^{1}H–^{13}C heteronuclear single–quantum correlation (HSQC) and 1D selective gradient total correlation spectroscopy (TOCSY) were employed to assign the major components. Moreover, different liquid samples from FR HTC at 180, 200, 220, 240 °C within 1, 4, 8, 12, 24 h were analyzed quantitatively by NMR (qNMR, maleic acid as the internal standard substance) to study the reaction pathway of FR HTC. Moreover, the determination and quantification of main compounds in the stock process water will provide valuable information for waste water disposal and treatment plant.

2. Experimental section

2.1. Materials

FR was collected from furfural factory located in Gaoping (Shanxi province in China). Deashed furfural residue (D-FR) was prepared as prior described [2]. Maleic acid, 5-HMF (99%), and glycerol were purchased from Aladdin Reagent Company (Shanghai). Levulinic acid (LA, 98%) was obtained from Sinopharm Chemical Reagent Co., Ltd. Deuterium oxide (D_2O, 99.9 atom% D) was supplied by Cambridge Isotope Laboratory. Double distilled water was used in all experiments. All chemicals were analytical grade and used as received.

2.2. Hydrothermal carbonization

The stock process water was collected from HTC processes on FR at different reaction temperatures (180, 200, 220 and 240 °C) and different reaction times (1, 4, 8, 12 and 24 h) following the previously described procedure [2]. All these HTC experiments were repeated at least twice. The obtained supernatants were kept at 4 °C in the refrigerator for NMR analysis. The liquid samples were denoted as D-FR-T-t, where T refers to HTC temperature (°C) and t is reaction time (hours, h).

2.3. Stock process water analysis

NMR data were acquired on a Bruker AV-III 400 MHz NMR spectrometer (9.39 T) equipped with Samplecase at

room temperature, using a 5 mm standard band probe. The ^{1}H and ^{13}C NMR were obtained at frequency of 400.13 MHz and 100.61 MHz, respectively. The chemical shifts of ^{1}H and ^{13}C NMR were referenced to 6.29 ppm and 132.0 ppm of maleic acid.

^{1}H NMR parameters are: "noesygppr1d" pulse is used for H_2O peak suppression and the quantitative analysis, P1 = 9.51 μsec, PLW1 = 18 W, AQ = 2.56 s, D1 = 30.0 s (for quantitative analysis), D8 = 0.015 s, DS = 4, NS = 8. ^{13}C NMR parameters are: zgpg 30 program, P1 = 9.50 μsec, PLW1 = 84 W, AQ = 1.36 s, D1 = 2.0 s, DS = 4, NS = 40 k. "Cosygpmfqf" program was used for obtaining COSY spectra. "Hsqcedetgpsisp 2.3", a phase-sensitive ge-2D multiplicity-edited $^{1}H-^{13}C$ HSQC, was utilized to differentiate CH/CH_3 (the positive signal of red color) and CH_2 (the negative signal of blue color) along with getting C–H correlation information. 1D selective gradient TOCSY experiment was employed after doing a ^{1}H NMR, and the shaped pulse "selmlgp" was applied on the peak at the O1 position, with the mixing time D9 = 90 ms. Quantitative ^{1}H NMR was operated according to our earlier work with maleic acid as a standard reference in D_2O [24]. The liquid samples (0.5 mL) were injected into a 5 mm NMR tube with 0.1 mL of standard solution loaded in a coaxial insert.

3. Results and discussion

3.1. Analysis of major compounds in HTC stock process water

The liquid phase obtained from thermochemical conversion of carbohydrates, lignin and real biomass is commonly very complex and rich in organic compounds [17,19]. FR used in this study mainly consists of cellulose and lignin, i.e. the water soluble compounds generated from HTC process of FR would be very complicated. As a result, it is insufficient to analyze the composition of these samples by just one NMR technique or spectrum. Therefore, besides 1D NMR, 2D NMR techniques were also employed to identify correlations between protons and carbons of all major components in stock process water. The structures proposed on the basis of the NMR obtained from the HTC procedure were confirmed by ^{1}H NMR spectra of the pure authentics. Firstly, all the samples were analyzed by ^{1}H NMR (Fig. S1–S2, Supplementary data). According to these ^{1}H NMR data, the stock process water containing most different species is that obtained at 240 °C after 1 h (Fig. 1), and this is therefore chosen as a representative sample to analysis and assign main components from the HCT treatment.

There are five major sharp peaks at 9.34, 8.19, 7.42, 6.56 and 6.29 ppm in the down field region. Firstly, the internal standard substance, maleic acid at δ = 6.29 ppm, was known and assigned, leaving four signals to be assigned with the aid of other NMR techniques. For the peaks at 7.42 (1H, d, J = 3.6 Hz) and 6.56 ppm (1H, d, J = 3.6 Hz), as shown in Fig. S3, they share the same coupling constant and with COSY cross-coupled signals (Fig. S5), which confirm that they are neighboring protons. The signal located at 9.34 ppm, on the other hand, only show self-correlation in COSY. The peak at 9.34 ppm (1H, s) is linked with carbon at (δ = 180.4 ppm), as shown in the HSQC spectrum (Fig. S6), which suggests it to be an aldehyde group. The peaks at 7.42 and 6.56 ppm correlate with the carbon signals at 134.5 (CH) and 110.9 ppm (CH) respectively as seen from the HSQC spectrum in Fig. S6. Combined with the ^{13}C NMR and HSQC spectra in Fig. S4 and S6, the peaks located at 161.3 and 151.7 ppm are from quaternary carbon atoms. Therefore, we suggest these three signals, namely 9.34, 7.42, and 6.56 ppm, to originate from 5-HMF. To confirm that the signals indeed originate from 5-HMF further NMR experiments, including 1D selective gradient TOCSY and the use of an authentic sample, were carried out.

1D selective gradient TOCSY is an excellent technique for the analysis of mixtures of minor components, and to elucidate the complete backbone in spin-coupling network. This technique demands no special hardware and no extra calibrations, and has been applied to identify the minor components in the lipid fraction of milk samples [26]. According to our 1D selective gradient TOCSY spectrum (Fig. 2a), the two peaks mentioned above (7.42 and 6.56 ppm), are in the same spin-system as the peak at 4.59 ppm (2H, s) and hence belong to the same molecule. The carbon signal at 56.1 ppm, could be linked to a hydroxyl group based on its down-field shift. All the information of the protons and carbons can be found in Fig. S3–S6. Compared with the spectrum of an authentic 5-HMF sample (Fig. S7), it confirms that 5-HMF (^{1}H, δ = 9.34, 7.42, 6.56 and 4.59 ppm) was produced during HTC as a major product. This is in agreement with the previous studies on biomass or cellulose HTC, where 5-HMF was detected in the liquid phase by HPLC [12]. Under the present hydrothermal condition, 5-HMF is a reactive molecule and can self-condensate into a dimer or oligomer, which could result in the formation of humins in process water and grafted into biochar [27].

From the ^{1}H and COSY spectra in Fig. S8 and S10, it can be deduced that the single peak at 8.19 ppm likely belongs to formic acid, since this signal was only self-correlated. HSQC experiment (Fig. S11) allowed site-specific assignment of the covalently bonded ^{1}H and ^{13}C pairs by the cross peak detected at 8.19 and 166.8 ppm (CH in formic acid). From the ^{1}H spectra in Fig. S8, the signals at 3.25 and 1.98 ppm are singlets, and combined with the peaks at 48.9 ppm (CH_3) and 20.5 ppm (CH_3) from the ^{13}C and HSQC spectra (Fig. S11), these two signals can be assigned to methanol (3.25 ppm) and acetic acid (1.98 ppm), respectively. These three compounds have previously been detected in the HTC process water by HPLC, GC–MS, and ^{1}H NMR [15,28,29].

There are more peaks in the interval from 2 to 3 ppm detectable in the ^{1}H NMR spectrum (Fig. 1). The triplet peaks at 2.76 ppm (2H, t, J = 6.3 Hz) and 2.49 ppm (2H, t, J = 6.3 Hz) share the same J value (Fig. S12) and correlate with each other as shown in the COSY spectrum (Fig. S14). When exciting the peak at 2.76 ppm, the signals at 2.49 ppm and 2.12 ppm increase in intensity according to the 1D selective gradient TOCSY spectrum (Fig. 2b). The connected

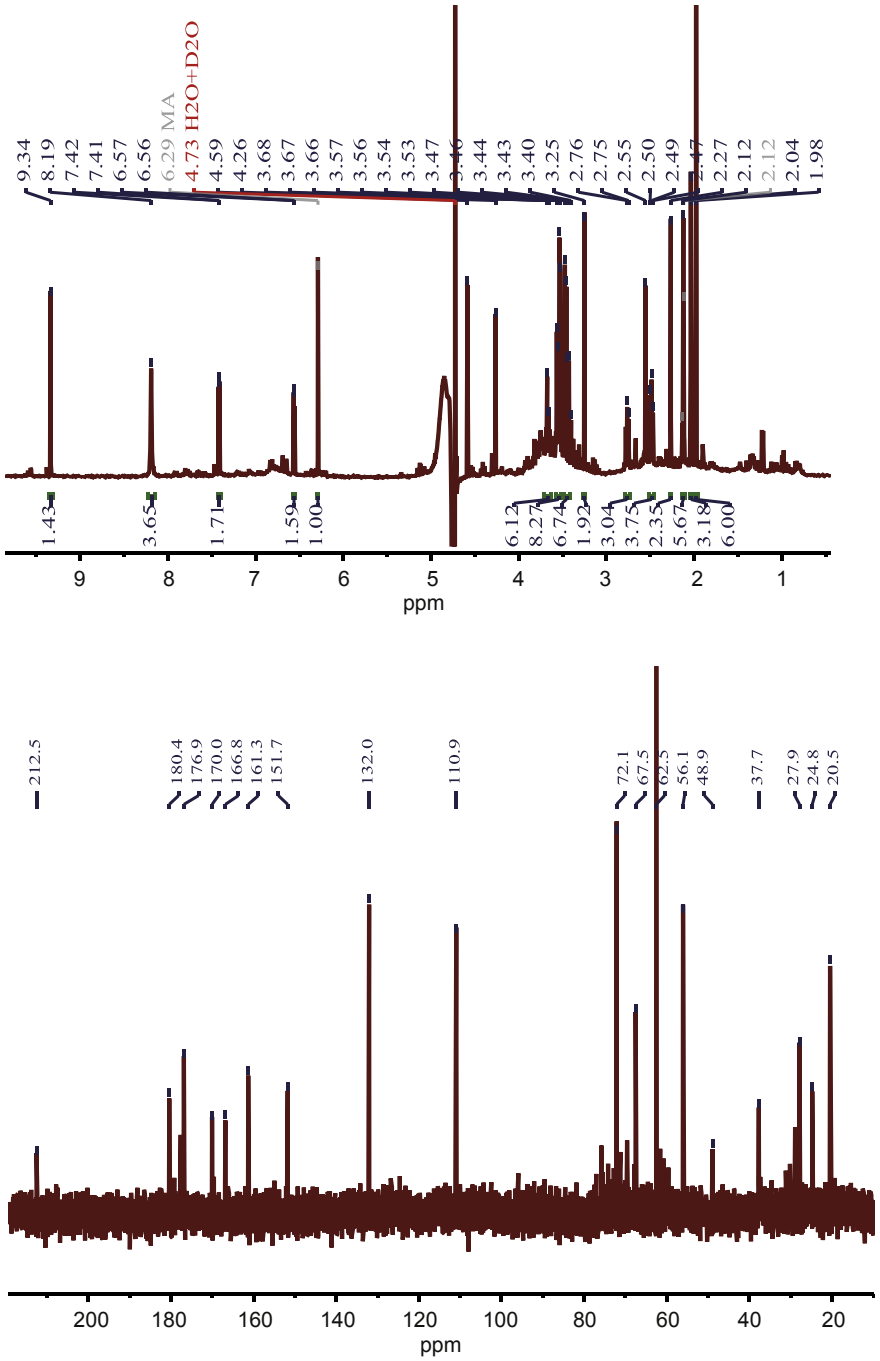


Fig. 1. ^{1}H and ^{13}C NMR spectra of compounds in process water from D-FR by HTC at 240 °C and 1 h.

carbons are located at 37.7 ppm (CH_2, 2.76 ppm), 27.9 ppm (CH_2, 2.49 ppm) and 29.0 ppm (CH_3, 2.12 ppm) respectively according to HSQC spectrum (Fig. S15). Thus, together with the ^{1}H NMR spectrum of an authentic sample (Fig. S16), these peaks can be assigned to LA. Our present spectra confirms that the rehydration reaction of 5-HMF to LA and formic acid takes place under the reaction conditions, and hence agree with the mechanism for hydrothermal lignocellulose biomass conversion [30].

Notably, there are two distinctive peaks in the region between 3.30 and 4.00 ppm showing doublet of doublets splitting (dd) (Fig. 1). The one at 3.55 ppm (1H, dd, $J = 11.7, 4.3$ Hz) has the same coupling constant ($J = 11.7$ Hz) as the signal at 3.46 ppm (1H, dd, $J = 11.7, 6.6$ Hz; Fig. S17). In addition both signals are correlated with the signal at 3.67 ppm (1H, m) as confirmed by the 1D selective gradient TOCSY (Fig. 2c) and COSY (Fig. S19) spectra. HSQC spectrum (Fig. S20) also demonstrates that there are two CH_2 groups ($\delta = 3.55$ ppm, 62.6 ppm; 3.46 ppm, 62.6 ppm) and one CH group ($\delta = 3.68$ ppm, 72.1 ppm) in this product. Combining all these NMR results (Fig. S17–S20), we can assign this compound to glycerol, and confirm this by matching with the standard

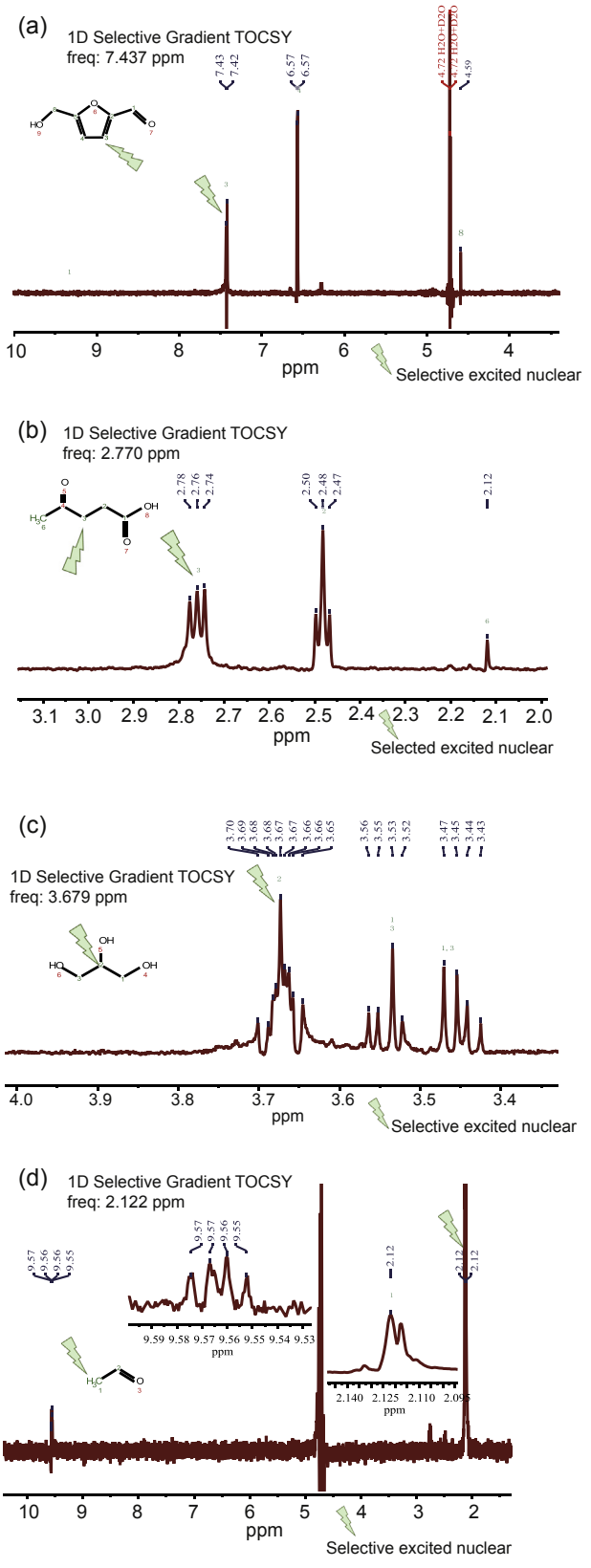


Fig. 2. 1D selective gradient TOCSY spectra of (a) 5-HMF, (b) LA, (c) glycerol and (d) acetaldehyde in HTC process water of D-FR-240-1.

spectrum of glycerol listed in Fig. S21. Two reaction routes to obtain the glycerol have been proposed in the field of bio-refinery. First, the glycerol could be prepared from glucose by hydrogenolysis under the H_2 pressure of 4 Mpa [31]. However, our present HTC conditions are mild and different from this hydrogenation process, and a reduction reaction of carbohydrate is less likely to take place. Secondly, glycerol is the main byproduct of biodiesel preparation through hydrolysis or alcoholysis of triglyceride [32]. We carried out a series of experiments and disclosed that the glycerol was prepared from hydrolysis of trace amount of lipid, probably triglyceride in FR (see the supplementary data and latter section for more details).

There are two additional singlets at 2.04 ppm and 4.26 ppm respectively (Fig. S22), and they only show self-correlation in COSY (Fig. S25). Selectively excited resonances at 2.04 ppm were set to differentiate all proton resonances from the rest in this compound, and only the peak at 4.26 ppm appears in the 1D selective TOCSY spectrum (Fig. S23). HSQC (Fig. S26) demonstrates that there are one CH_3 (δ = 2.04 ppm, 24.90 ppm) and one CH_2 (δ = 4.26 ppm, 67.57 ppm) groups in this molecule. Compared it with the spectrum of hydroxyacetone in reference, it can be confirmed identity [33]. Hydroxyacetone can be produced by multiple ways such as dehydration of glycerol or dehydrogenation of polyols and sugar alcohols, and had been detected on the primary cellulose pyrolysis reactions [34].

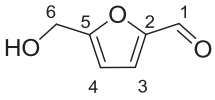
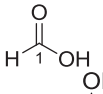
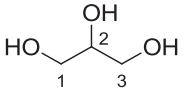
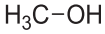
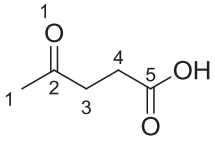
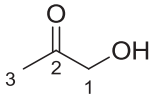
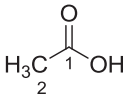
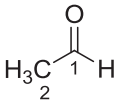
The peak at 2.12 ppm is not a regular singlet as seen on Fig. S27, and it was found to correlate with CH_3 (29.05 ppm) in the HSQC spectrum (Fig. S30). A correlation between 2.12 ppm and 9.56 ppm was also found in the COSY spectrum (Fig. S29). 1D selective gradient TOCSY experiment was carried out to make further identification, and there is an observably but very weak peak appearing at 9.56 ppm (quartet) in Fig. 2d. From these spectra, we can assign the peak at 2.12 ppm and 9.56 ppm to arise from acetaldehyde [35].

At this stage, the main detectable compounds in stock process water of FR HTC can be listed (Table 1). However, there are also many low concentrated compounds with weak signal intensity or heavily overlapped peaks, which could not be assigned accurately, such as the protons in aromatic (6.0−8.5 ppm) and in aliphatic (0.7−1.9 ppm) regions.

3.2. Quantitative analysis of stock process water samples

The former section assigned the main components in stock process water qualitatively, a quantitative analysis of these detected compounds is highly desirable as this could clarify the possible HTC pathway. QNMR measurement can be easily conducted by peak integrals relative to a reference signal in a properly acquired spectrum, and maleic acid has earlier been found as a suitable internal standard [36]. Therefore, the QNMR was carried out for the stock process water obtained under different HTC conditions, and the obtained ^1H spectra were shown in Fig. S1 and S2. The calculated concentration of the main compounds is presented in Figs. 3 and 4, respectively.

Table 1
Detected compounds in stock process water and their ^{1}H and ^{13}C chemical shifts.

Compound	Chemical structure	Atom number	Chemical shift (ppm)	
			^{1}H	^{13}C
5-HMF		1	9.34 (s)	180.4
		2	–	161.3
		5	–	151.7
		3	7.42 (d)	134.5
		4	6.56 (d)	110.9
		6	4.59 (s)	56.1
Formic acid		1	8.19 (s)	166.8
Glycerol		2	3.69 (m)	62.6
		1,3	3.46/3.55 (dd)	72.2
Methanol		1	3.25 (s)	49.0
Levulinic acid		2	–	212.5
		5	–	176.9
		4	2.76 (t)	37.7
		3	2.49 (t)	27.9
		1	2.12 (s)	29.0
Hydroxyacetone		1	4.26 (s)	67.6
		3	2.04 (s)	24.9
Acetic acid		2	1.98 (s)	20.5
		1	–	170.0
Acetaldehyde		1	9.56 (m)	NA
		2	2.12 (s)	30.1

NA: not available.

As shown in Fig. 3, the amount of detected compounds, except formic acid, increased with the temperature increasing from 180 °C to 220 °C, but these trends change when the temperature was increased to 240 °C. For example, some compounds including 5-HMF, formic acid and hydroxyacetone disappeared at 240 °C. In Becker's [12] research, the 5-HMF originated from cellulose HTC reached the maximum concentrations at 230 °C, and after treatment at 250 °C there is a significant decrease for 5-HMF concentration in the process water. In this study, the 5-HMF is disappeared in longer reaction time. The formic acid can be generated from both hydrolysis of 5-HMF and lignin HTC [37]. The concentration of methanol, LA and acetic acid increased as the reaction temperature was elevated, and the concentration of glycerol reached a plateau between 220 and 240 °C.

According to our previous ^{13}C solid state NMR and XPS analysis results of FR HTC biochar at 200 °C and 8 h, the composition on its surface changed obviously but the bulk ones had no big difference with FR. The partial hydrolysis of cellulose has taken place at this stage, and left the lignin almost intact [2]. The 5-HMF was detected in the ^{1}H NMR spectra from the HTC treatment under 240 °C, which is a key intermediate for dehydration product of D-glucose under hydrothermal condition, and also detected in the cellulose HTC process [38]. The increased content of 5-HMF from 4.23 (180 °C, 8 h) to 15.88 mg/g FR (220 °C, 8 h) might be due to the fast cellulose hydrolysis under these high reaction temperature. While 5-HMF was not observed at the liquid phase collected at 240 °C, which suggests a faster self-condensation, rehydration and graft reactions to surface of solid biochar. This agrees well with the research of Titirici et al. [10] which consider that the HTC of cellulose followed a process similar to classical pyrolysis. The increased concentration of organic acids (LA and formic acid) at high temperature would promote intermediate conversion and accelerate the HTC process [8]. The amount of glycerol remains largely the same over the process and increased from 5.81 mg/g FR at 180 °C to 25.15 mg/g FR at 220 °C, and then kept constant from 220 °C to 240 °C. As for the protons of aromatic compounds in the region 6.0–8.5 ppm and aliphatic compounds in 0.7–1.9 ppm, the concentration in stock process water increased with the increase of reaction temperature. Interestingly, these aromatic protons are not detected by ^{1}H NMR in stock process water of cellulose HTC [7]. On this basis we attribute these compounds to the degradation of lignin fraction in FR.

Additional experiments were designed to unravel the formation of glycerol. The experimental details, the ^{1}H spectral results of stock process water, and the QNMR data about glycerol in stock process water are provided in supplementary data. Firstly, there is no glycerol detected in the HTC stock process water of cellulose HTC catalyzed by H_2SO_4, spherical carbon with $-SO_3H$ groups, and lignosulfonic acid (Fig. S31). Accordingly, glycerol is not generated from the cellulose in FR under present HTC condition. Quantitative data of glycerol content in stock process water of FR and cellulose mixtures with different ratios, exhibited that the amount of glycerol was proportional to the weight ratio of FR in the mixture (Fig. S32). Thus, we could confirm that the glycerol is formed from the lipids in FR, because that hydrolysis of trace amount of triglyceride in FR probably produces the glycerol as a high thermal stable compound.

According to our previous work, 240 °C is required for the preparation of biochar with a higher degree of aromatization [2]. Quantitative ^{1}H spectra of HTC stock process water from 240 °C at different reaction times (Fig. 4 and Fig. S2) showed that there were obvious differences in the compositions of these liquid samples. The concentration of 5-HMF and formic acid decreased from 1 to 4 h, and then disappeared after 8 h. While other components, such as glycerol, methanol, LA, and

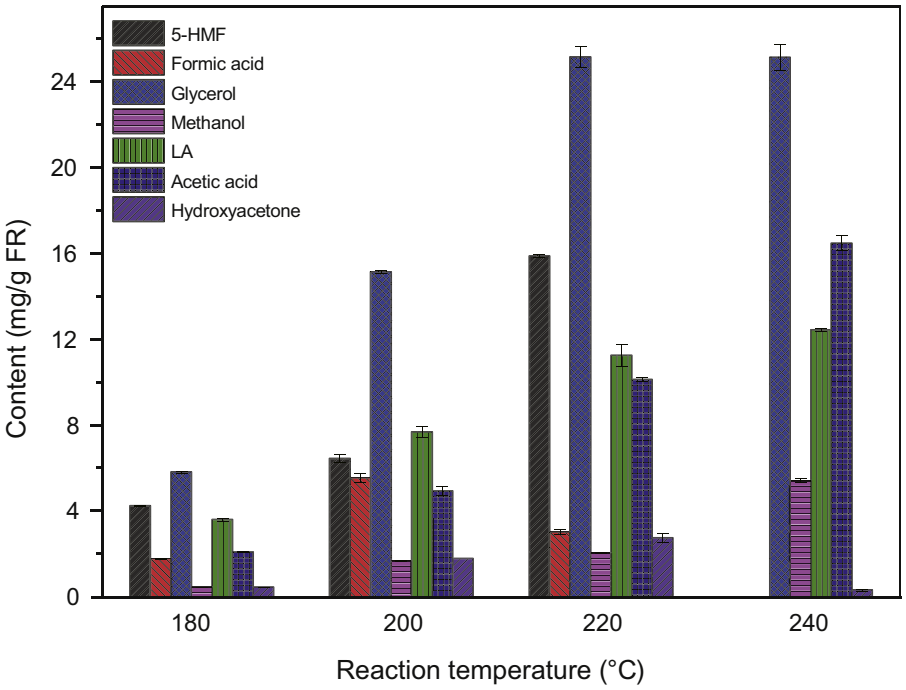


Fig. 3. Concentration of main compounds in HTC process water at different reaction temperatures (180–240 °C) and 8 h.

acetic acid increased with HTC reaction time because of their thermal stability during HTC process.

From the characterization of the obtained biochar the optimal starting conditions for the HTC reaction was found to be 1 h at 240 °C and that HTC process was almost accomplished within the first 8 h. In the liquid phase, the main conversions in the HTC process also occurred within 8 h and the cellulose is converted into both 5-HMF and finally biochar, and 87% and 20% of the cellulose remained in biochar obtained at 1 h and 4 h, respectively [2]. The liquid sample collected at 1 h gave the highest 5-HMF content, and with increasing reaction times, 5-HMF could not be detected after 4 h. This result is according with a faster conversion rate (both decomposition and conversion to biochar) than its formation

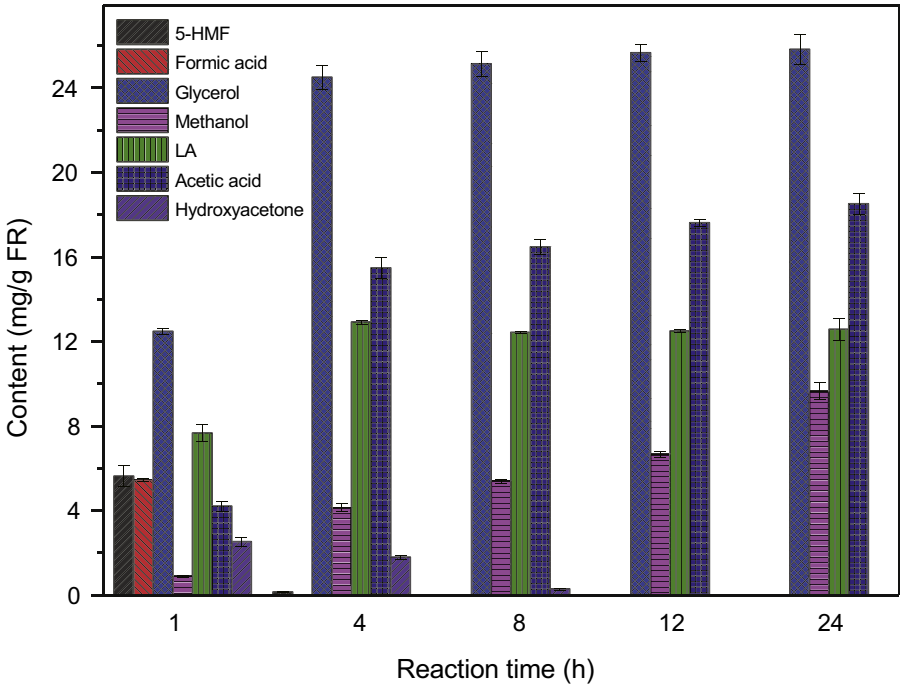


Fig. 4. Concentration of main compounds in HTC process water of different reaction times (1–24 h) at 240 °C.

rate [10]. The 5-HMF in the liquid phase disappeared completely within 8 h, at the same time, the cellulose in FR was completely consumed. The increase of methanol and acetic acid content indicated that the side reaction occurred in the HTC process as the reaction time rising.

3.3. Reaction pathways of the HTC

Associate with the biochar characterization in our previous report and the present analysis of liquid phase composition, it is possible to propose the pathways for biochar formation from FR under hydrothermal conditions. The main conversions of FR during HTC are shown in Fig. 5, where the blue frames denote the composition in the solid, the green frames show the compounds found in stock process water, and the orange frame represents the gas phase. Moreover, the solid lines indicate the reaction pathway, while the dotted lines represent the possible reaction path. At the reaction temperature of 240 °C, a part of the cellulose is hydrolyzed and dehydrated to give 5-HMF as reported [12]. The major amount of the 5-HMF could graft and convert to biochar directly or rehydrated to give LA and formic acid, and disappeared after 8 h reaction of HTC [7]. The amount of methanol and acetic acid, as byproducts of HTC, increased with the reaction time. Although the lignin in the solid part showed weak reactivity, the detected aromatic and aliphatic compounds in stock process water suggest that lignin is partly decomposed during HTC through demethylation, dealkylation as well as cleavage of β-O-4 bonds [39]. In the final process water, the compounds remained are LA, glycerol, methanol and acetic acid. The low molecular weight specie formic acid, hydroxyacetone will degrade to CO_2 and H_2O. Furthermore, there are also a certain amount of the carbon which end up in the gas fraction, which has not been quantified or analyzed in this research.

4. Conclusions

Both routine and advanced NMR technologies were employed to investigate the main components in the stock process water from FR HTC. The detectable compounds inside were 5-HMF, formic acid, methanol, acetic acid, levulinic acid, glycerol, hydroxyacetone and acetaldehyde. The concentrations of these compounds changed in different HTC times and temperatures, and the finally remained compounds in process water were LA, glycerol, methanol and acetic acid. Based on the analysis of liquid compositions and our available data of solid biochar, reasonable reaction pathways during FR HTC were proposed: a) cellulose was decomposed completely

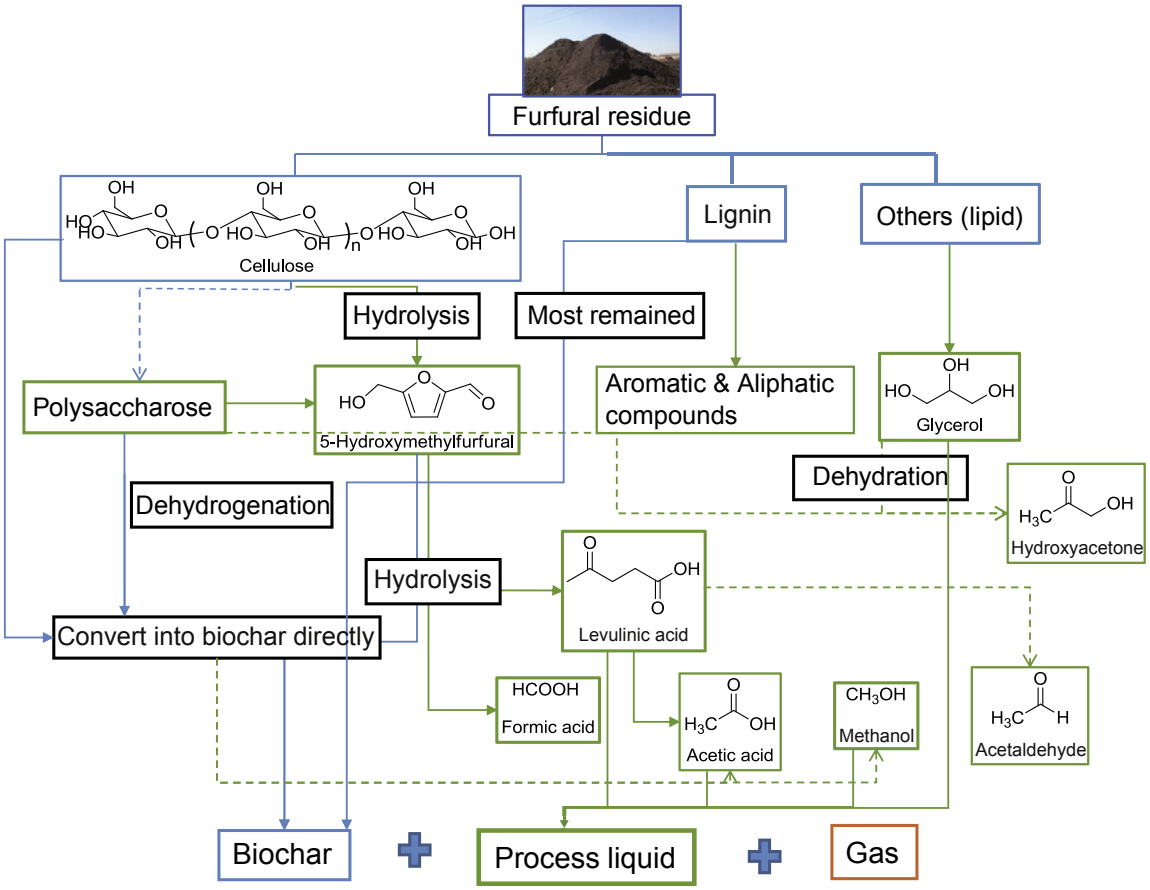


Fig. 5. The reaction pathways of FR during HTC hydrothermal carbonization. (Blue frames denote the solid composition and the green frames show the compound in process water. The orange frame represents the gas phase. Moreover, the solid lines indicate the reaction pathway, and the dotted lines represent the possible reaction path).

and convert into both liquid phase and solid biochar. The part of cellulose is hydrolyzed and dehydrated to 5-HMF, and further into formic acid and LA; b) most of lignin in FR showed weak reactivity and remained in final biochar, and only partial lignin decomposition into aromatic and aliphatic compounds in stock process water. This work demonstrates the reactions during FR HTC, but more importantly it provides a novel NMR method to analysis the complicate reaction system.

Conflict of interest

There is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.gee.2017.08.006.

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